

# **PREDICTION OF INTERFACIAL PROPERTY OF LIQUID SYSTEMS BY MULTISCALE MODELLING**

Rakesh Chandran P

A Dissertation Submitted to  
Indian Institute of Technology Hyderabad  
In Partial Fulfillment of the Requirements for  
The Degree of Master of Technology



भारतीय प्रौद्योगिकी संस्थान हैदराबाद  
Indian Institute of Technology Hyderabad

Department of Chemical Engineering

June, 2014

### **Declaration**

I declare that this written submission represents my ideas in my own words, and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

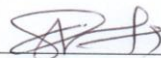


Rakesh Chandran P

CH12M1013

## Approval Sheet

This thesis entitled "Prediction of Interfacial Property of Liquid Systems by Multiscale Modelling" by Rakesh Chandran P is approved for the degree of Master of Technology from IIT Hyderabad.



Dr. Chandra Shekhar Sharma; Asst. Professor

Examiner



Dr. Debaprasad Shee; Asst. Professor

Examiner



Dr. Saptarshi Majumdar; Asst. Professor

Adviser

Dr. Kishalay Mitra; Asst. Professor

Co-Adviser

Dr. Raja Banerjee; Asst. Professor

Chairman

## **Acknowledgements**

I would like to express my sincere gratitude for all who supported me wholeheartedly during my M Tech Program.

I am very much grateful to my guide Dr. Saptarshi Majumdar for all his encouragement and support during the research work and as a person who takes care the feelings of his students. I also would like to thank to my co-guide Dr. Kishalay Mitra for his countless support and inspiration. I am very much grateful to all the faculty members at Department of Chemical Engineering, IIT Hyderabad and my committee members: Dr. Chandra Sekhar Sharma, Dr. Debaprasad Shee, and Raja Banerjee of Department of Mechanical Engineering.

I would like to thank Himanshu Goel and Pinaki Swain for all their help which helped me a lot during this work.

Dedicated to

My Parents.

## Abstract

Binary immiscible liquid mixtures when mixed together tend to form an interface. To predict interfacial tension; it requires a detailed treatment of fundamental forces like Van der Waals, electrostatic interactions and hydrogen bonding among molecules. However in mesoscopic model all these detailed forces information result in the form of repulsive interaction parameters  $a_{ii}$  and  $a_{ij}$ . In the present effort, the interfacial tension has been predicted based on different self-repulsive interaction parameters of each component for liquid-liquid system and also, interfacial tensions for different kinds of liquid-liquid systems at different temperatures are predicted using Dissipative Particle Dynamics (DPD). Isothermal compressibility of pure components is used to find the like-like repulsion parameter whereas the solubility parameter is used to evaluate the unlike interaction parameter. The temperature variation of isothermal compressibility and solubility parameter affects the interaction parameter and introduces the temperature effect into the system. The methodology is applied to water-alkane, water-aromatic and non-water systems and comparisons are made with experimental studies reported in the literature. The proposed formalism not only reproduces the temperature dependence of interfacial tension but also matches with the absolute values with reasonable accuracy.

## Nomenclature

$a_{ii}$  Self-repulsive interaction parameters of i bead

$a_{jj}$  Self-repulsive interaction parameters of j bead

$a_{ij}$  Repulsive interaction parameters between i & j

$\sigma$  Fluctuation amplitude

$\rho$  Dimensionless bead density

$V_b$  Volume of bead

$K_B$  Boltzmann constant

$T$  Temperature

$\delta$  Solubility Parameter

$K_T$  Isothermal compressibility

$\chi$  Flory Huggins parameter

$R$  Gas constant

$\Delta G^C$  Combinatorial contribution in Gibbs energy

$\Delta S_{\text{mix}}$  Entropy of mixing

$\Delta G_{\text{mix}}$  Gibbs energy of mixing

$\Delta G^R$  Residual contribution in Gibbs energy

$\Delta S^C$  Combinatorial contribution in entropy of mixing

$C$  Cohesive energy density

$\Delta_{\text{vap}}u$  Heat of vaporization

$V_L$  Molar volume

$f_i$  force on particle  $i$

$m_i$  Mass of particle  $i$

$a_i$  Acceleration of particle  $i$  Time

$u^E$  Total energy of mixture

$\sigma_{DPD}$  Stress in DPD units

$P_{xx}$  Pressure force along  $x$  axis

$w_D$  Weight function

$v_{ij}$  Relative velocity

$f_i^D$  Dissipative force

$f_i^R$  Random force

$f_i^C$  Conservative force

$\mu$  Chemical Potential

$\Gamma$  Thermodynamic Factor



## Figures

<b>Fig 1.1</b>	Multiscale Modelling.....	2
<b>Fig 7.2.1</b>	Temperature dependence of interfacial tension for water-heptane system.....	22
<b>Fig 7.2.2</b>	Temperature dependence of interfacial tension for water-octane system.....	22
<b>Fig 7.2.3</b>	Temperature dependence of interfacial tension for water-benzene system.....	23
<b>Fig.7.2.4</b>	Temperature dependence of interfacial tension for water-toluene system.....	24
<b>Fig.7.2.5</b>	Temperature dependence of interfacial tension for water-cyclohexane system.....	25
<b>Fig.7.2.6</b>	Temperature dependence of interfacial tension for ethylene glycol-tetra decane system.....	25
<b>Fig 7.2.7</b>	Variation F-H parameter with temperature for water-heptane system.....	27
<b>Fig 7.2.8</b>	Water- Heptane System FH Method.....	28
<b>Fig 7.2.9</b>	Water- Octane System FH Method.....	28
<b>Fig.7.2.10</b>	Water-Benzene System FH Method.....	29

## Tables

<b>Table 7.1</b>	Interfacial tension for Partially Miscible Mixtures.....	19
<b>Table 7.2.1</b>	Classification of different systems studied.....	21
<b>Table 7.2.2</b>	Temperature Dependence of systems.....	26
<b>Table 7.3.1</b>	Diffusion coefficients of benzene-cyclohexane system.....	30
<b>Table 7.3.2</b>	Diffusion coefficients using DPD.....	30
<b>Table 7.4.1</b>	Properties of individual Components.....	31
<b>Table 7.4.2</b>	Properties of components at different temperatures.....	32

# Contents

Declaration.....	ii
Approval Sheet .....	iii
Acknowledgements .....	iv
Abstract.....	vi
Nomenclature.....	vii
Figures.....	ix
Tables.....	x
<b>1 Introduction.....</b>	<b>1</b>
1.1Multiscale Modelling.....	1
1.2 Prediction of thermo physical properties.....	2
<b>2 Problem Definition.....</b>	<b>4</b>
<b>3 Literature Review.....</b>	<b>3</b>
3.1Interfacial Tension.....	3
3.2 Temperature Dependence of interfacial Tension.....	6
3.3 Diffusivity Prediction.....	6
<b>4 Methodology.....</b>	<b>7</b>
4.1 Dissipative Particle Dynamics.....	7
4.2 Molecular Dynamics.....	10

<b>5 Liquid Models.....</b>	<b>12</b>
5.1 Regular Solution Theory.....	12
5.2 Flory-Huggins Theory.....	13
 <b>6 Prediction of Liquid Properties.....</b>	 <b>14</b>
6.1 Prediction of Interfacial Tension.....	14
6.1.1. Calculating DPD interaction parameter.....	14
6.2 Prediction of temperature dependence of interfacial tension.....	16
6.2.1. By calculating DPD mutual interaction parameter through solubility parameter.....	16
6.2.2. By calculating DPD mutual interaction parameter through Flory-Huggins parameter.....	16
6.3 Prediction of Mutual diffusion coefficient.....	17
6.4 Simulation details.....	18
<b>7 Results and Discussions.....</b>	<b>19</b>
7.1 Prediction of interfacial tension with DPD model.....	19
7.2 Prediction of temperature dependence of interfacial tension.....	21
7.2.1. By calculating DPD mutual interaction parameter through Solubility parameter.....	22
7.2.2 By calculating DPD mutual interaction parameter through Flory-Huggins parameter.....	27
7.3 Mutual Diffusion coefficient prediction.....	30
7.4 Properties of individual components.....	31
<b>8 Conclusions.....</b>	<b>34</b>
<b>9 Scientific Contribution.....</b>	<b>35</b>
References.....	36

# Chapter 1

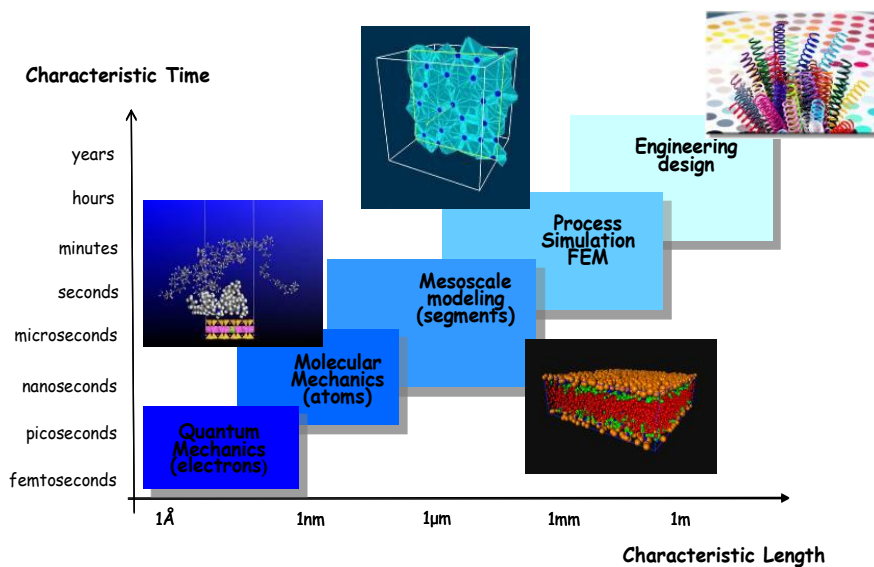
## Introduction

### 1.1 Multiscale modeling.

There have been rapid improvements in modeling of physical and chemical process at atomistic level over the past two decades mainly because of the increase in computer speed and memory, improved theoretical methods based in quantum or statistical mechanics etc. Multiscale modeling can effectively replace experiments and can give insight to various processes. Theory and modeling methods can be classified into four groups depending on the length and time scales to which they apply.

- a) Electronic scale in which matter is made up of fundamental particles like electron and is described by quantum mechanics.
- b) Molecular scale in which matter is made up of atoms which obeys laws of statistical mechanics.
- c) Mesoscale in which matter is regarded as a cluster of atoms.
- d) Continuum level in which matter is regarded as a continuum macroscopic laws like equations of continuity and momentum conservation can apply.

# MULTI-SCALE MODELING



Ref:- COSMO-RS and process simulation: from physical properties to environmental impact ,by Maurizio Fermeglia & Sabrina Priel 3

**Fig 1.1 Multiscale Modelling**

## 1.2 Prediction of thermo physical properties

Prediction of thermo physical properties like interfacial tension and diffusivity by different modeling methods is of great interest [1]. Both these properties are function of temperature an accurate prediction of temperature dependence is a challenging problem. Molecular level techniques have limited length and time scales. A proper mesoscale method can solve this problem to a great extent.

Dissipative Particle Dynamics (DPD) can be used for the prediction of interfacial tension. In broad sense, the term “interface” includes any boundary that separates two different phases. However, it is generally associated with the liquid-liquid case and interfacial tension is the force per unit length exerted on the interface between two immiscible liquids. In the past few decades, computer simulation methods such as molecular dynamics and Monte Carlo method have played a huge role in reducing the number of experiments [2,3]. However, it is not practically realizable to study a macroscopic system by detailed atomistic simulation due to the length and time scale involved. In recent years, Dissipative Particle Dynamics (DPD) introduced by Hoogerbrugge and Koelman[4], has emerged as a popular coarse grained method. DPD enables us to reach length scale, where molecular level fluctuations are still important but at the same time inaccessible by atomistic simulation.

# **Chapter 2**

## **Problem Definition**

- 1) Prediction of various thermo physical properties (interfacial tension, diffusivity, solubility parameter etc) of liquids.
- 2) Formulate a general protocol for prediction of properties through meso-scale modeling.
- 3) Predict the temperature dependence of properties accurately.
- 4) Reduction of computational time by using coarse graining.



# Chapter 3

## Literature Review

### 3.1 Interfacial Tension

Interfacial tension is an important equilibrium property which strongly influences the dynamics of a multiphase system. Prediction of interfacial tension is of great interest in industrial applications like preparing emulsions, surfactants etc. There are some studies which predicts interfacial tension using dissipative particle dynamics In recent years, Dissipative Particle Dynamics model was successfully applied to study many important physical phenomena such as phase separation between immiscible liquids and polymer systems [5-6], morphology evaluation [7], reduction of interfacial tension through surfactants [8]. But all of them predicts interfacial tension for a few systems and could not provide a general protocol for prediction of variety of systems.

DPD model was introduced by Hoggerbuge and Koelman [4] in 1992. In DPD model all the detailed force information is taken care by the repulsive interaction parameter  $a_{ii}$  and  $a_{ij}$ . In 1997 Groot et.al [9] introduced a relationship between the self-repulsive conservative force parameter  $a_{ii}$  and inverse of isothermal compressibility and also Groot et. al [9] formed a relation between repulsion parameter  $a_{ij}$  and Flory-Huggins parameter  $\chi_{ij}$ . Here Groot et.al [9] made a basic assumption that  $a_{ii}=a_{jj}$  which means the interaction between beads of i-i is equal to the interaction between beads of j-j. Maiti et.al [10] followed this method and predicted interfacial tension for a few number of systems. In 2007 Travis et al. [11] formed a new relation for calculating the interaction parameters by relating with Scatchard Hildebrand Regular Solution Theory (RST). He came up with a relation to get interaction parameter using solubility parameter and they eliminated the basic assumption of  $a_{ii}=a_{jj}$ .

### 3.2 Temperature Dependence of Interfacial Tension

Interfacial Tension is a function of temperature and accurate prediction of interfacial tension with temperature is a challenging problem. Though several researchers have studied the temperature dependence of interfacial tension experimentally, a general agreement on this is yet to be reached. Ataev [12] has measured the interfacial tension of water and hydrocarbons and found a positive coefficient of  $\frac{d\sigma}{dT}$  which contradicts Antonov rule. Rafati *et al.* [13] have reported a linear decrease of interfacial tension with temperature for mixtures of ethylene glycol and aliphatic alcohols. A rather interesting observation comes from the works of Vázquez *et al.* [14] and Villers *et al.* [15] where the interfacial tension between water and lower alcohols is reported to be linearly decreasing with temperature and in case of higher alcohols, the existence of non-linearity is reported. In 2013 Mayoral *et al.* [16] have predicted the interfacial tension for water-cyclohexane and water-benzene system by adopting the parameterization method proposed in the seminal work of Groot *et al.* [9]. In this work they were able to match the slope of the straight line but the intercept values were in poor agreement. Our main objective is to predict the temperature dependence of interfacial tension by the method suggested by Goel *et al.* [17].

### 3.3 Diffusivity prediction

Mutual diffusion coefficient or cross diffusion coefficients is an important property which gives an idea about the miscibility of the system. There have been literatures in predicting diffusivity of liquids in polymer [18]. Liu *et al.* [19] has calculated Fick's diffusivities through molecular dynamics(MD) simulation for liquid-liquid systems. Fick's diffusivities are obtained from Maxwell-Stefan (MS) diffusivities. Mutual diffusion experiments measure Fick's diffusion coefficients, while molecular simulation provides MS diffusivities. A thermodynamic factor is required to convert MS diffusivity into Fick's diffusivity. DPD can also give Fick's diffusivity but not as accurate as MD. Groot *et al.* [9] has given an equation to predict DPD diffusivity which shows that DPD diffusivity prediction will be an order of magnitude different.

# Chapter 4

## Methodology

### 4.1 Dissipative Particle Dynamics

Dissipative Particle Dynamics (DPD) is an off lattice, discrete particle method for modeling mesoscale systems. The Dissipative Particle Dynamics method was introduced by Hoogerbrugge and Koelman [4] in 1992. DPD model have the following advantages

- It exhibits hydrodynamic behavior.
- It has thermal fluctuations that can drive Brownian motion.
- It is cheap to simulate.

In the DPD approach, the forces due to individual solvent molecules is lumped together to yield effective friction and a fluctuating force between moving fluid elements. While this approach does not provide a correct atomistic description of the molecular motion, it has the advantage that it does reproduce the correct hydrodynamic behavior on long length and time scales.

Like standard molecular dynamics (MD) algorithm, DPD also involves the updation of positions and momenta of all the particles by numerically solving the equations of motion.

$$\frac{d\vec{r}_i}{dt} = \vec{v}; \frac{d\vec{p}_i}{dt} = \vec{f}_i$$

Where  $\vec{x}_i$  is the position and  $\vec{v}_i$  is the velocity of particle  $i$  and  $\vec{F}_i$  is the force experienced by it due to its interaction with all other particles.

The difference is that, in addition to the conservative force  $\vec{f}_{ij}^c$  acting between particles, the total force on a particle i now also contains a dissipative force  $\vec{f}_{ij}^D$  and a random force  $\vec{f}_{ij}^R$ .

$$\vec{f}_i = \sum_{j \neq i} \vec{f}_{ij}^C + \vec{f}_{ij}^D + \vec{f}_{ij}^R$$

The conservative force  $\vec{f}_{ij}^c$  can, be derived from a pair potential that acts between particles i and j.

$$\begin{aligned} \vec{f}_{ij}^C &= a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \frac{\vec{r}_{ij}}{r_{ij}} & (r_{ij} < r_c) \\ \vec{f}_{ij}^C &= 0 & (r_{ij} \geq r_c) \end{aligned}$$

Where  $a_{ij}$  is interaction parameter between i and j ,  $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ ;  $r_{ij} = |\vec{r}_{ij}|$  and  $r_c$  is an interaction cut-off range parameter

The dissipative force corresponds to a frictional force that depends both on the positions and the relative velocities of the particles. The motion of the molecules within each bead dissipates energy and opposes relative motion of the beads.

$$\vec{f}_{ij}^D = -\gamma \omega_d(r_{ij}) (\vec{r}_{ij} \cdot \vec{v}_{ij}) \vec{r}_{ij}$$

Where  $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$  is the relative velocity  
 $\gamma$  is a friction coefficient  
 $\omega_d$  is a distance dependent weight function that is zero for  $r_{ij} > r_c$

The random motion of the molecules within each bead tends to exert a fluctuating force and it is of the form

$$\vec{f}_{ij}^R = -\sigma \omega_r(r_{ij}) \theta_{ij} \vec{r}_{ij}$$

$\sigma$  is a fluctuation amplitude  
Where  $\omega_r$  is a distance dependent weight function that is zero for  $r_{ij} > r_c$   
 $\theta_{ij}$  is a Gaussian distributed random number with zero mean and unit variance

The strength of the dissipative force and random force cannot be chosen independently and is fixed by the fluctuation-dissipation theorem. These two components of the forces together act as the equivalent of thermostat in MD. So, the natural statistical ensemble in case of DPD is that of canonical ensemble. Following Groot et.al [9] the weight function takes the form

$$\omega_d = \left(1 - \frac{r_{ij}}{r_c}\right)$$

The dissipative and random are coupled through fluctuation-dissipation theorem [20].

$$\omega_d(r_{ij}) = [\omega_r(r_{ij})]^2$$

$$\sigma^2 = 2\gamma K_B T$$

Generally a value of 4.5 for frictional coefficient and Fluctuation amplitude value of 3 provides good results in literatures [9,10].

Dissipative particle dynamics model is used for large variety of applications.

- Simulating systems such as polymers, biopolymers, lipids, emulsions and surfactants.
- Complex fluids near interfaces: micro fluidics, slip of liquid flow past surfaces.
- Surfactants related applications including paints and coatings, emulsions, dispersions, bio and nanotechnology etc.

## 4.2 Molecular Dynamics

Molecular Dynamics simulation is a technique for computing the equilibrium and transport properties of a classical many-body system [2] . The essence of molecular modeling resides in the connection between the macroscopic world and the microscopic world provided by the theory of statistical mechanics. The atoms and molecules are allowed to interact for a period of time, giving a view of the motion of the atoms. In the most common version, the trajectories of atoms and molecules are determined by numerically solving the Newton's equations of motion for a system of interacting particles, where forces between the particles and potential energy are defined by molecular mechanics force fields.

The molecular dynamics simulation method is based on Newton's second law or the equation of motion,  $F=ma$ , where  $F$  is the force exerted on the particle,  $m$  is its mass and  $a$  is its acceleration. From knowledge of the force on each atom, it is possible to determine the acceleration of each atom in the system. Integration of the equations of motion then yields a trajectory that describes the positions, velocities and accelerations of the particles as they vary with time. From this trajectory, the average values of properties can be determined. There are large numbers of commercial force field available such as OPLS, Trappe, UFF, CHARMM, AMBER, GROMOS, Dreiding, COMPASS etc.

$$F_i = m_i a_i$$

$$F_i = m_i \frac{\partial^2 r_i}{\partial t^2}$$

Where  $F_i$  is the force on particle  $i$ ,  $m_i$  is mass of particle  $i$ ,  $a_i$  is acceleration on particle  $i$ , and  $t$  represent time.

Numerous numerical algorithms have been developed for integrating the equations of motion. Some are listed below.

- 1) Verlet algorithm
- 2) Leap-frog algorithm

3) Velocity Verlet

4) Beeman's algorithm

Thermostats are available to add and remove energy and mainly to control temperature of the system in the canonical ensemble. The thermostat is used to control temperature fluctuations such as velocity rescaling, the Nose-Hoover thermostat, Nosé-Hoover chains, the Berendsen thermostat, the Andersen thermostat etc. Similarly A variety of barostats are available to control the pressure of the system in the NPT ensemble such as Parrinello, Anderson, and Berendsen barostat.

At present, the atomistic simulation simulates smaller system of few atoms and covers smaller time scales in the range of nanoseconds. The greatest challenge for using atomistic simulation is the computational cost. However, increasing capacity of computing power will be able to tackle such issues.

# Chapter 5

## Liquid Models

### 5.1 Regular Solution Theory

Regular solution is defined as solution where the components mix with no excess entropy provided that there is no volume change of mixing. Scatchard and Hildebrand proposed a parameter Cohesive Energy Density (C) for the improvement of the theory. The parameter C is defined as

$$C = \frac{\Delta_{vap} u}{v^L}$$

Where the energy of complete vaporization is, is the molar volume of the liquid, C is the cohesive energy density. The cohesive energy density is defined as amount of energy needed to remove unit volume of molecule

The energy of a binary liquid mixture can be expressed as a quadratic function of volume fraction.

$$-(u_{liq} - u_{idealgas})_{mix} = \frac{c_{11}v_1^2x_1^2 + 2c_{12}v_1v_2x_1x_2 + c_{22}v_2^2x_2^2}{x_1v_1 + x_2v_2}$$

This can be written in terms of volume fractions  $\phi_1$  and  $\phi_2$  as

$$-(u_{liq} - u_{idealgas})_{mix} = (x_1v_1 + x_2v_2)(c_{11}\phi_1^2 + 2c_{12}\phi_1\phi_2 + c_{22}\phi_2^2)$$

$c_{12}$  is taken as the geometric mean between  $c_{11}$  and  $c_{22}$

$$c_{12} = \sqrt{c_{11}c_{22}}$$

$$-(u_{liq} - u_{idealgas})_{mix} = (x_1v_1 + x_2v_2)\phi_1\phi_2(\delta_1 - \delta_2)^2$$



Where  $\delta_1, \delta_2$  are the Hildebrand solubility parameters which is nothing but the square root of cohesive energy density [21]. Hansen proposed a 3D solubility parameter [22].

## 5.2 Flory-Huggins Theory

The Flory Huggins theory is based on a lattice approach. The regular solution theory, applied to molecules of similar sizes where as Flory-Huggins theory applied to molecules having difference in their volume like polymer solutions. The Gibbs energy of mixing consists of enthalpy and entropy contributions. Entropy contributed cannot be neglected. There are two terms (1) Combinatorial contribution  $\Delta G^C$  (2) Residual contribution  $\Delta G^R$ .

$$\Delta G_{\text{mix}} = \Delta G^C + \Delta G^R$$

Flory and Huggins also showed that if the amorphous polymer and the solvent mix without any energetic effect (Athermal behavior) the change in Gibbs energy and entropy of mixing are given by.

$$\Delta G^C/RT = \Delta S^C/R = -(N_1 \ln \phi_1 + N_2 \ln \phi_2)$$

The residual term will depend on the interactions between solvent molecules and polymer segments, and also on the composition of the system.

$$\Delta G_{\text{mix}}/RT = (N_1 \ln \phi_1 + N_2 \ln \phi_2) + \chi \phi_1 \phi_2 (N_1 + N_2).$$

$$\chi = V (\delta_1 - \delta_2)^2 / RT$$

Where  $\chi$  is known as Flory Huggins parameter, R is gas constant, T is Temperature, and  $\delta$  is Hildebrand solubility parameter. The Flory Huggins parameter  $\chi$  is responsible for the energy of the mixing for polymer and solvent molecules.

# Chapter 6

## Prediction of liquid properties

### 6.1 Prediction of Interfacial Tension

When two immiscible liquids are mixed together they will not mix with each other and will form an interface as thin as possible. At interface, there are unresolved forces between different liquids, which cause tension at the boundary. The interfacial tension can be rightly predicted by considering the unresolved forces involved at interface. As mentioned by Maiti et. al.[10] interfacial tension can be computed by integrating the difference between normal and tangential stresses across the interface (normal to the x-direction). In order to create x-normal interfaces it is common practice to increase the system extent in the x-direction. This simple alteration makes a x-normal interface have a smaller surface area, which leads to a lower free energy.

$$\sigma_{DPD} = \int \left[ \bar{p}_{xx}(\bar{x}) - \frac{1}{2} (\bar{p}_{yy}(\bar{x}) + \bar{p}_{zz}(\bar{x})) \right] d\bar{x}$$

$$\sigma_{real} = \frac{k_B T}{r_c * r_c} \sigma_{DPD}$$

#### 6.1.1 Calculating DPD interaction parameter

To find the interaction parameters between the beads a combined approach of Groot et.al [9] and Travis *et al* is[11] been used. However, the assumption of equality of like-like interaction parameter ( $a_{11} = a_{22}$ ) taken by Groot et al [9] is omitted. The isothermal compressibility of each component to calculate the repulsion parameter between similar beads and use solubility parameters to calculate the repulsion parameter between dissimilar beads.

The like-like repulsion parameter  $a_{ii}$  is obtained by using the relation,

$$a_{ii} = \left[ \kappa_i^{-1} (N_{m,i} - 1) / 2\alpha\rho_i \right] k_B T, \quad i = 1, 2$$

Where  $N_{m,i}$  is the degree of coarse graining for species  $i$ ,  $\alpha$  is a numerical constant,  $\rho_i$  is the number density of species  $i$  and  $\kappa_i^{-1}$  is the dimensionless isothermal compressibility of the species which is related to the physical isothermal compressibility  $\kappa_{T,i}$  as  $\kappa^{-1} = 1 / \rho k_B T \kappa_{T,i}$ ,  $\rho$ , being the number density of the molecules.

The interaction parameter between different types of beads,  $a_{12}$ , is obtained using the relation

$$(\delta_1 - \delta_2)^2 = -r_c^4 \alpha \left[ \rho_1^2 a_{11} + \rho_2^2 a_{22} - 2\rho_1 \rho_2 a_{12} \right]$$

Where  $\delta_i$  is the solubility parameter of pure component  $i$ ,  $r_c$  is the cut-off radius and  $a_{ij}$  is the interaction parameter between component  $i$  and  $j$ .

The coarse grain model is based on averaging of molecular volume and interaction among molecules. For water and Benzene, coarse grain model W[5][1]B[1][1] is been chosen. The reason behind choosing W[5][1]B[1][1] coarse grain model is due to the size and individuality of benzene structure. Here W[5][1] indicates one water bead consist of five water molecule and B[1][1] indicates one benzene bead of one benzene molecule. The benzene molecule is aromatic compound having a ring structure, which cannot be cut or broken. Therefore, it has to be taken as a single molecule bead. The molecular volume of five water molecules becomes  $150 \text{ \AA}^3$  and one benzene molecule is  $148 \text{ \AA}^3$ . So the average molecular volume of bead is kept  $149 \text{ \AA}^3$ . Based on this bead volume, we calculated the  $a_{12}$  repulsive interaction parameters.

## 6.2 Prediction of temperature dependence of interfacial tension

### 6.2.1 By calculating DPD mutual interaction parameter through solubility parameter

Goel et.al [17] predicted interfacial tension of 45 systems using a combined approach of Groot et.al [9] and Travis et.al. [11] The same method has been followed for finding the interaction parameters. The temperature effect in the system can only be introduced through the interaction parameters. We must have the information of isothermal compressibility of individual components at different temperatures to estimate the like-like interaction parameter. Similarly, we must have the solubility parameters for both the components at different temperatures to calculate the unlike repulsion parameter. Mayoral et.al [16] has done a temperature dependence study using DPD. Experimental values of interfacial tension at different temperatures in taken from literatures [23-25].

### 6.2.2 By calculating DPD mutual interaction parameter through Flory-Huggins parameter

Groot et.al [9] formulated a method to find unlike interaction parameters using Flory-Huggins interaction parameter and is been followed by Maiti et.al [10].

$$a_{ij} = a_{ii} + 3.27 \chi_{ij}$$

They assumed the like like interaction parameters to be equal. In this work the assumption of like like interaction parameters is been removed and the following equation is been used for calculating the unlike interaction parameter.

$$a_{ii}^* = a_{ii} + 3.27 \chi_{ij}$$

$$a_{jj}^* = a_{jj} + 3.27 \chi_{ij}$$

$$a_{ij} = \frac{a_{ii}^* + a_{jj}^*}{2}$$

We calculated Mutual interaction parameter by using  $a_{ii}$  and  $a_{jj}$  individually and average the values to get  $a_{ij}$

### 6.3 Prediction of mutual diffusion coefficient

To describe diffusive mass transport in liquid mixtures, generalized Fick's law and the Maxwell-Stefan theory are often used. For describing multicomponent diffusion in liquids, the Maxwell-Stefan (MS) approach is often advocated. The key point of this approach is that the driving force for diffusion of component  $i$  (i.e., the chemical potential gradient  $\Delta\mu_i$ ) is balanced by a friction force, resulting in the following equation.

$$\frac{-1}{RT} \nabla \mu_i = \sum_{j=1, j \neq i}^n \frac{x_j (u_i - u_j)}{D_{ij}}$$

in which  $R$  and  $T$  are the gas constant and absolute temperature, respectively. The friction force between components  $i$  and  $j$  is proportional to the difference in average velocities of the components,  $(u_i - u_j)$ . As generalized Fick's law and the MS theory describe the same physical process, it is possible to relate the corresponding transport coefficients. The mutual diffusion coefficient,  $D_{12}^{\text{Fick}}$ , can be written as a product of a thermodynamic factor,  $\Gamma$ , and the Maxwell-Stefan diffusion coefficient,  $D_{12}^{\text{MS}}$ .

$$D_{12}^{\text{Fick}} = \Gamma D_{12}^{\text{MS}}$$

Thermodynamic factor  $\Gamma_{ij}$  is defined by

$$\Gamma_{ij} = \delta_{ij} + x_i \left( \frac{\partial \ln \gamma_i}{\partial x_j} \right)_{T, p, \Sigma}$$

$\delta_{ij}$  is the Kronecker delta, and  $\gamma_i$  is the activity coefficient of component  $i$ . The symbol  $\Sigma$  is used to indicate that the differentiation is carried out while keeping constant the mole fractions of all other species except the  $n$ -th.

Wilson activity coefficient model is used for calculation in this work.

It is given by

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right)$$

Where  $\Lambda_{12}$  and  $\Lambda_{21}$  are Wilson parameters which are taken from literatures [26].

#### 6.4 Simulation details

The simulations are carried out using the DPD module of Material Studio suite 6.0 [27]. All the inputs to the solver are provided in dimensionless units. Dimensionless number density  $\rho^* = 3$  is used in the simulation, so that we can use the DPD equation of state. The strength of dissipative and random forces is kept at 4.5 and 3, respectively in order to maintain the temperature at  $k_B T = 1$ . Dimensionless time step, i.e.,  $\Delta t^* = 0.02$  was used during the simulation. Velocity-Verlet algorithm is used for numerically solving the equation of motion, with slight modification to account for the velocity dependent drag force in the DPD model. 6000 DPD particles were used in the simulation and the dimension of the simulation domain were  $L_x^* = 20$ ,  $L_y^* = L_z^* = 10$ . Periodic boundary conditions were imposed in all direction

Similarly, Molecular Dynamics simulations were carried out on Material Studio 6.0 using Forcite module [28] of Accelrys. Periodic cells are constructed with 25 Å sides by using amorphous cell construction module. After construction, the system has been energy minimized and geometry optimized. A time step of one femtosecond was used. The equilibration period of 50 picoseconds (NVT dynamics) was used followed by production run (NPT dynamics) for 150 picoseconds. Also COMPASS forcefield [29] is used for interatomic interactions in molecular dynamic simulations. All the results are analyzed with the help of Forcite analysis.

# Chapter 7

## Results and Discussions

### 7.1 Prediction of interfacial tension with DPD model

In this chapter, we would like to discuss briefly about result obtained by DPD simulations. To validate new approach for determining self-repulsive interaction parameters. We have validated the interfacial tension for different liquid-liquid system with published experimental data. It includes different polar and nonpolar molecules with different chemical structure and properties.

**Table 7.1 Interfacial tension for Partially Miscible Mixtures**

<b>System</b>	<b>Coarse Graining Model</b>	<b>Predicted Interfacial Tension at 25°C dyn/cm</b>	<b>Interfacial tension experimental (Temp.) dyn/cm</b>
Water-Tridecane	W[7][1]TD[1][2]	55.55	51.14(25°C)
Water-Tetradecane	W[2][1]TR[1][7]	54.49	51.55(25°C)
EG-Heptane	EG[1][1]H[1][2]	19.44	16.02(20°C)
Glycerol-Heptane	G[2][1]H[1][1]	35.6	31.07(20°C)
Glycerol-Nonane	G[2][1]N[1][1]	28.85	30.53(20°C)
DMSO-Decane	DM[3][1]D[1][1]	9.07	9.20(23°C)
FM –Decane	FM[2][1]D[1][3]	29.77	28.33(23 <sup>0</sup> C)
Water-Pentadecane	W[2][1]PD[1][7]	52.76	51.2(25°C)

EG: Ethylene Glycol, FM: Formamide, DMSO: Dimethyl sulfoxide

- In older studies, coarse graining was handled only for few liquid-liquid systems and these studies only include the prediction of the interfacial tension for few water & alkane system. In our approach, we tend to build a protocol for different liquid-liquid systems based on their specific underlying chemistry and physics.
- Also, a preferred beading was found to match a particular experimental data.
- The main advantage of this approach is to reduce a simplified assumption  $a_{ii}=a_{jj}$  and to predict the interfacial tension for large number of system.
- The unit for interfacial tension is in dyn/cm.
- In some of the cases, due to the unavailability of experimental data for interfacial tension at specific temperature, we have predicted interfacial tension at 25°C. As an example. Glycerol- Heptane system, we have predicted interfacial tension at 25°C with a value of 35.6, but the experimental value 31.07 is available at 20°C. As temperature increases, the interfacial tension tends to decrease.
- Here Ethylene glycol is modeled as single molecule in a single bead due to its characteristics of having intra hydrogen bonding among its molecule. For this specific reason, we must use a single molecule of Ethylene glycol in a bead.
- In case of Glycerol, DMSO, Formamide molecules, their nature have intermolecular hydrogen bonding among themselves, which results in 2-3 molecules in a bead.



## 7.2 Prediction of temperature dependence of interfacial tension

### 7.2.1 By calculating DPD mutual interaction parameter through solubility parameter

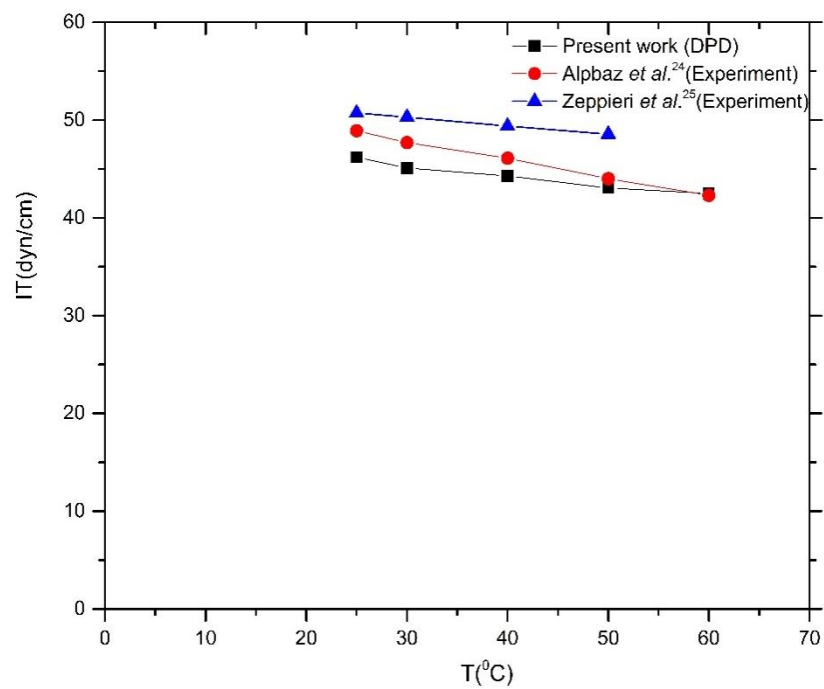
We have evaluated interfacial tension for different types of systems and made the comparison between the present method, method suggested by Mayoral *et al* [16] and the experimental data available in the literature. All the systems are studied at 50:50 composition of DPD particles and within a temperature range of 25°C – 60°C. The various systems undertaken for study are divided into different categories as shown in Table 7.2.1

**Table 7.2.1 Classification of different systems studied**

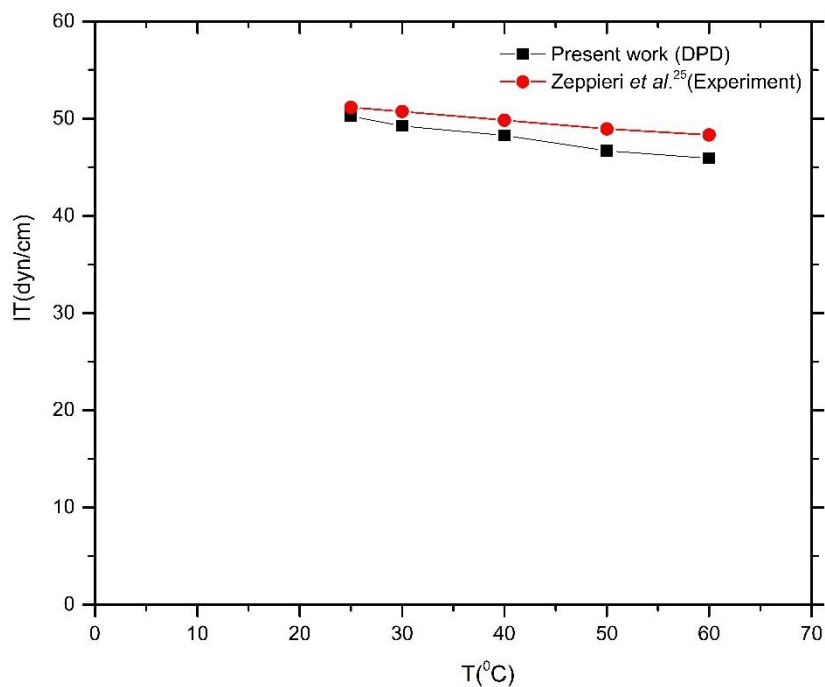
1. Water-alkane systems	Water-Heptane, Water-Octane
2. Water-aromatics systems	Water-Benzene, Water-Toluene
3. Other systems	Water-Cyclohexane, Ethylene glycol-Tetradecane

#### WATER-ALKANE SYSTEMS:

In Figure 7.2.1 and 7.2.2 we have shown the temperature dependence of interfacial tension of water-heptane and water-octane systems obtained from present DPD simulation along with the earlier experimental results. The temperature range considered for this study is from 25°C – 60°C, same as that considered in the experimental studies. It can be seen that our simulation results are in close match with the experiments. As expected, interfacial tension decreases almost linearly with temperature



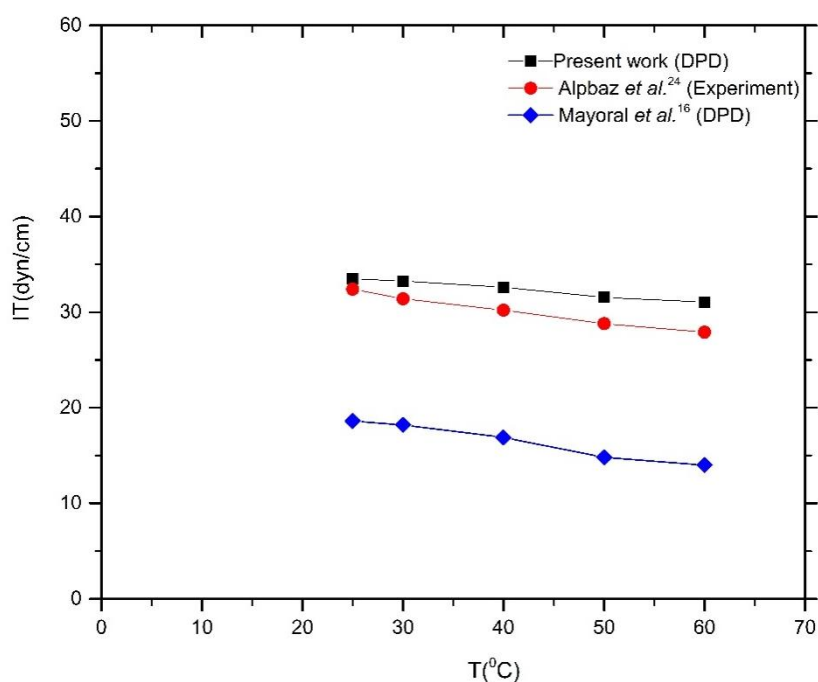
**Fig.7.2.1 Temperature dependence of interfacial tension for water-heptane system.**



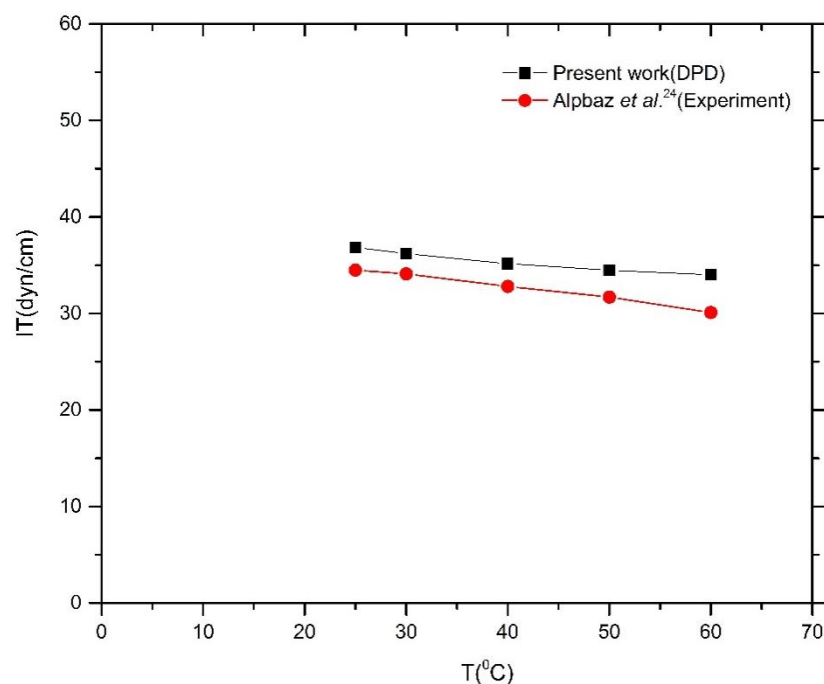
**Fig.7.2.2 Temperature dependence of interfacial tension for water-octane system.**

## WATER-AROMATICS SYSTEMS:

Figure 7.2.3 and 7.2.4 shows the comparison of DPD prediction of interfacial tension with that of experimental measurements for water-benzene and water toluene systems. For water-benzene system, we have also made comparison with earlier DPD work of Mayoral *et al.*[16] in which they have matched the slope of the linear relationship but not the absolute values. Like the earlier case, simulations done by the present effort have good agreements with the experimental findings.



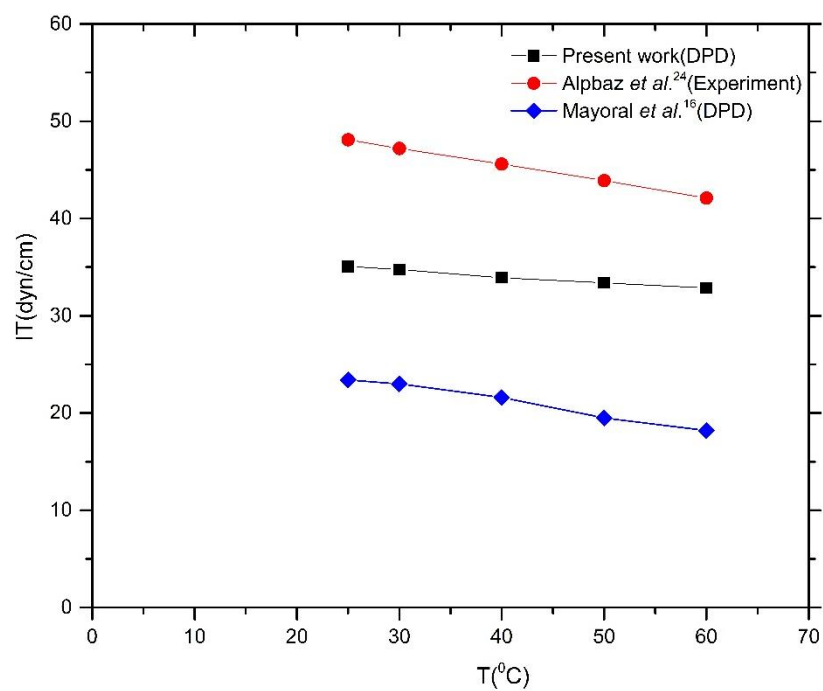
**Fig.7.2.3 Temperature dependence of interfacial tension for water-benzene system.**



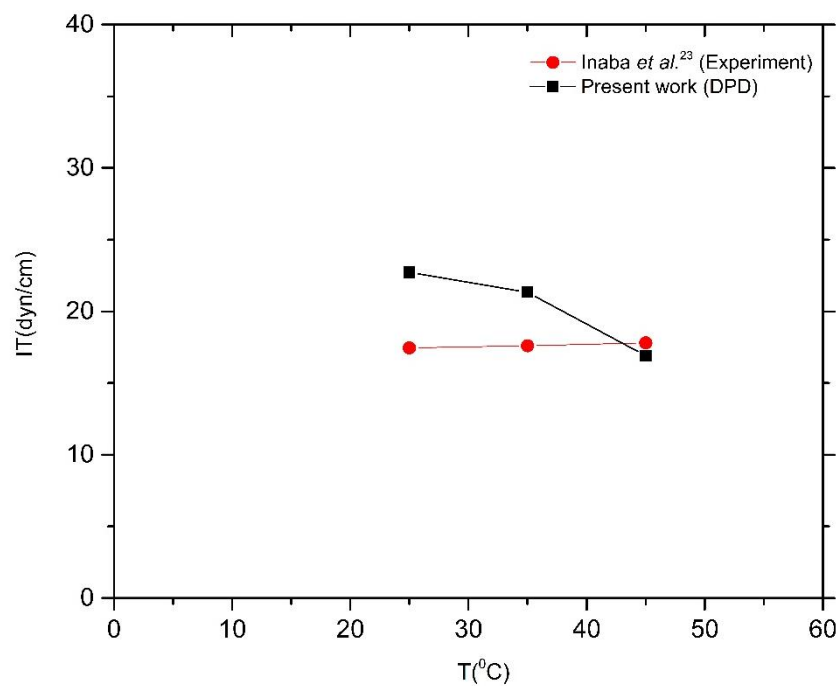
**Fig.7.2.4 Temperature dependence of interfacial tension for water-toluene system.**

#### OTHER SYSTEMS:

We have investigated the case of water-cyclohexane system, which has also been studied by Mayoral *et al.* [16] and the comparison of both the results with experiments is shown in Figure 7.2.5. It can be observed that results of present study are more close to the experimental data whereas Mayoral and co-workers [16] have only matched the slope. In order to test the range of applicability of our present formalism, we wanted to simulate different kinds of systems. But the lack of experimental values of interfacial tension limits the number of cases. However, we did try for one non-water system i.e. ethylene glycol-tetradecane, for which we found the required experimental values and the comparison is presented in Fig. 7.2.6. It can be observed that there is a slight increase in the value of interfacial tension with temperature in the experiments as reported by Inaba *et al.*[23] The slight increase in the experimental values may be within the experimental error and interfacial tension of this system can be considered as temperature independent.



**Fig.7.2.5 Temperature dependence of interfacial tension for water-cyclohexane system.**



**Fig.7.2.6 Temperature dependence of interfacial tension for ethylene glycol-tetra decane system.**

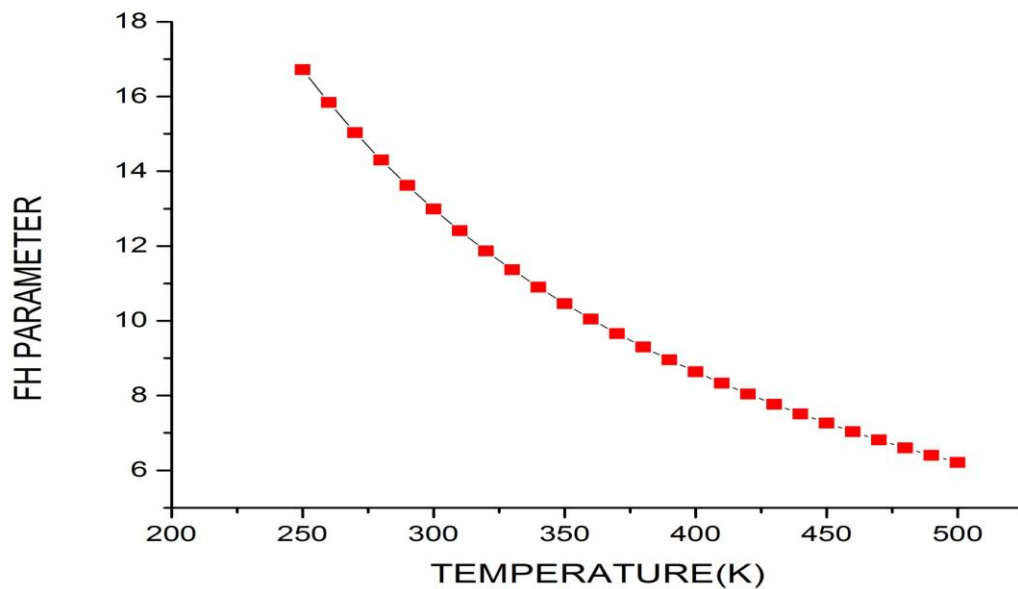
For each of the cases studied, the values of the intercept and the slope of a best fitted straight line are shown in Table II and comparisons are made with earlier experimental and DPD results. For water-heptane system, it can be seen that the reported slope is different in two experimental studies [24,25] and our results are more close to the more recent result reported by Zeppieri et al [25]. In case of water-octane system, both the intercept and slope are in good agreement with those of experiment.

**Table 7.2.2 Temperature Dependence of systems**

System	Experiment	DPD simulation (Mayoral et al.)	DPD simulations (present work)
Water-heptane	$\sigma = 52.7 - 0.171T$ $\sigma = 52.9 - 0.089T$		$\sigma = 48.45 - 0.103T$
Water-octane	$\sigma = 53.22 - 0.084T$		$\sigma = 53.12 - 0.102T$
Water-benzene	$\sigma = 36.0 - 0.139T$	$\sigma = (22.4 \pm 0.3) - (0.147 \pm 0.007)T$	$\sigma = 35.39 - 0.073T$
Water-toluene	$\sigma = 37.7 - 0.123T$		$\sigma = 38.64 - 0.083T$
Water-cyclohexane	$\sigma = 52 - 0.161T$	$\sigma = (27.76 \pm 0.3) - (0.161 \pm 0.005)T$	$\sigma = 36.62 - 0.064T$
Ethyleneglycol-tetradecane	$\sigma = 17 + 0.017T$		$\sigma = 30.5 - 0.291T$

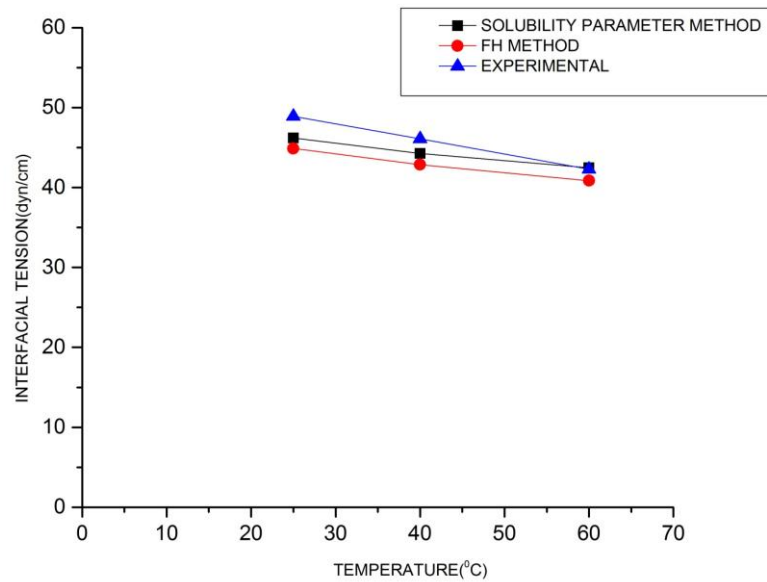
### 7.2.2 By calculating DPD mutual interaction parameter through Flory-Huggins parameter

By following Goel et.al [17] which calculates DPD parameter from solubility parameter we were able to match the accurate values of interfacial tension but not the slope so we calculated DPD interaction parameter through Flory-Huggins parameter and predicted the interfacial tension Flory-Huggins parameter will vary with temperature. Fig 7.2.7 shows the variation F-H parameter with temperature for water-heptane system.

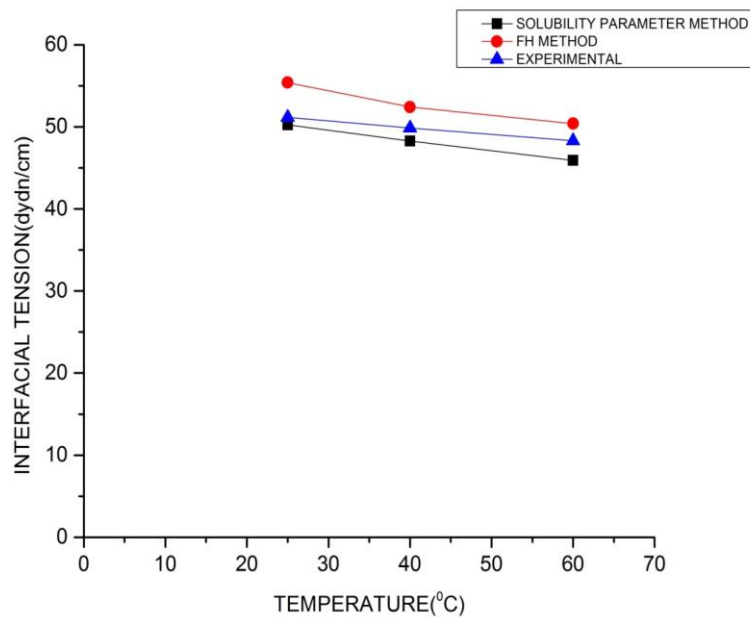


**Fig 7.2.7 variation F-H parameter with temperature for water-heptane system**

Fig 7.2.8 and 7.2.9 shows the comparison of interfacial tension predicted for water-heptane and water-octane by both methods.



**Fig 7.2.8 Water- Heptane System FH Method**

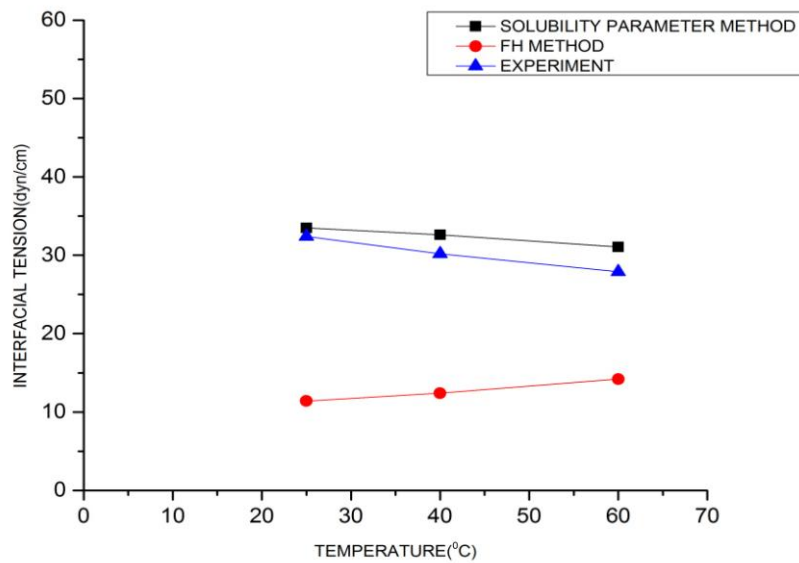


**Fig 7.2.9 Water- Octane System FH Method**



Calculating interaction parameter using solubility parameter is more accurate than using Flory-Huggins method. But for the case of water- heptanes system slope can be slightly modified by using FH method.

For the case of other liquid systems like Water- Benzene system the FH parameter method is not accurate. Fig 7.2.9 shows the case of Water-Benzene system.



**Fig.7.2.10 Water-Benzene System FH Method**

### 7.3 Mutual Diffusion coefficient prediction

Mutual diffusion coefficient is predicted by using both Molecular Dynamics and DPD. Molecular Dynamics simulation will give a good result for diffusion coefficient. Whereas DPD fails to predict diffusivity exactly. Table 7.3.1 and 7.3.2 shows the comparison of diffusion coefficients of benzene-cyclo hexane system for different compositions by using both MD and DPD and compared with experimental result [30].

**Table 7.3.1 Diffusion coefficients of benzene-cyclohexane system**

MOLE FRACTION OF CYCLO HEXANE	MS DIFFUSIVITY $\times 10^9 (\text{m}^2/\text{s})$	THERMODYN AMIC FACTOR	FICKS DIFFUSIVITY $\times 10^9 (\text{m}^2/\text{s})$	EXPT $\times 10^9$ ( $\text{m}^2/\text{s}$ )	% ERR OR	STANDARD DEVIATION
0.2	2.06	0.88	1.81	1.9	4.7	3.8
0.4	1.8	0.87	1.57	1.8	10.5	2.92
0.6	1.9	0.857	1.63	1.7	4.1	3.14
0.8	1.9	0.84	1.62	1.8	10	3.23

**Table 7.3.2 Diffusion coefficients using DPD**

MOLE FRACTION OF CYCLO HEXANE	MD DIFFUSIVITY $\times 10^9 (\text{m}^2/\text{s})$	DPD DIFFUSIVITY $\times 10^8 (\text{m}^2/\text{s})$	EXPT. $\times 10^9 (\text{m}^2/\text{s})$
0.2	1.81	2.22	1.9
0.4	1.57	2.04	1.8
0.6	1.63	2.2	1.7
0.8	1.62	2.1	1.8

## 7.4 Properties of individual components

Table 7.4.1 shows the properties of individual components such as density, isothermal compressibility, and solubility parameters of an individual component taken from various references [31-35] .

Component	Density (g/cm <sup>3</sup> )	Molecular volume (Å <sup>3</sup> )	Isothermal Compressibility (*10 <sup>-10</sup> Pa) (Temp)	Solubility Parameter (J/cm <sup>3</sup> ) <sup>1/2</sup>
Water	1	30	4.59	47.9
Formamide	1.134	66	4.11	36.65
Pentane	0.626	191.39	21.8	14.4
Heptane	0.6795	244.87	14.4	15.2
Octane	0.703	269.82	12.8	15.4
Nonane	0.718	296.4	11.8	15.6
DMSO	1.10	117.94	5.25	26.7
Dodecane	0.750	378	9.88	15.9
Decane	0.730	323.62	10.9	15.7
Hexane	0.650	218	16.8	14.9
Benzene	0.876	148	9.66	18.41
Glycerol	1.26	121.24	2.19	34.12
o xylene	0.88	200.34	8.11	18
m xylene	0.86	205	8.62	17.9
p xylene	0.86	205	8.59	17.9
Ethyl benzene	0.866	203.46	8.65	17.9
Toluene	0.866	176.68	9.12	18.3
Bromo benzene	1.495	174.38	6.68 (20°C)	19.94
Iodo Benzene	1.831	185.02	5.82	20.45
Chloroform	1.483	133.67	10.30 (20°C)	18.9
Ethylene glycol	1.11	92.5	3.40	33.70
Undecane	0.740	350.7	10.30	15.8
Tridecane	0.756	404.8	9.48	16.0
Chlorobenzene	1.10	112.56	7.71	19.61

The values of density, isothermal compressibility, solubility parameter and molar volume of pure components from literatures [36-40] used for finding the interaction parameters for temperature dependence of interfacial tension are listed in Table 7.4.2

**Table 7.4.2 Properties of components at different temperatures**

Component	Temperature (K)	Density (g/cm <sup>3</sup> )	Isothermal Compressibility (*10 <sup>-10</sup> Pa)	Solubility Parameter (J/cm <sup>3</sup> ) <sup>1/2</sup>	Molar Volume (A <sup>o3</sup> )
Water	298	0.997	4.59	46.84	30.8
	313	0.992	4.42	46.06	31.2
	333	0.983	4.45	44.88	31.69
Benzene	298	0.876	9.66	19.24	145.77
	313	0.856	10.9	18.78	148.48
	333	0.834	12.8	18.12	152.74
Toluene	298	0.861	9.11	18.3	177.32
	313	0.847	10.2	18.0	180.68
	333	0.828	11.8	17.4	184.29
Heptane	298	0.679	14.4	15.3	244.87
	313	0.666	16.4	14.96	249.72
	333	0.649	19.6	14.5	256.18
Octane	298	0.698	12.8	15.5	271.59
	313	0.686	14.5	15.19	276.29

	333	0.669	17.1	14.7	283.33
Cyclohexane	298	0.773	11.2	16.82	181.27
	313	0.759	12.8	16.35	184.54
	333	0.740	15.2	15.96	188.1
Ethylene Glycol	298	1.11	3.61	33.7*	92.5
	308	1.105	3.74	31.89*	93.1
	318	1.1	3.92	30.08*	93.6
Tetradecane	298	0.759	9.13	15.8	433.12
	308	0.752	9.73	15.6	437.15
	318	0.745	10.4	15.39	441.2

\* properties found by using molecular dynamics

# Chapter 8

## Conclusions

In this study, we suggested an a combine method of Groot et.al and Travis et.al to find the DPD interaction parameter. The assumption of equal self-conservative repulsive parameters  $a_{ii}=a_{jj}$  is not used and we calculated them individually .With this method We have validated interfacial tension for large number of immiscible and partially miscible systems. This method works nicely for the prediction of temperature dependence of interfacial tension. We have studied six different types of system for temperature dependence. We tried to predict the temperature dependence more accurately using FH parameter and found out that for some systems it is giving better results but in general Goel et.al method will give a nice prediction for interfacial tension for a variety of systems.

# Chapter 9

## Scientific Contribution

### Journals

Estimation of interfacial tension for immiscible and partially miscible liquid systems by Dissipative Particle Dynamics. Himanshu Goel, Rakesh Chandran P, Kishalay Mitra, Saptarshi Majumdar, Partha Ray, Chemical Physics Letters 600 (2014) 62–67

# References

- [1] M. Fermeglia. Molecular Modeling and process simulation: Real possibilities and challenge. Chem Biochem. Eng. Q. 17 (1) 19-29, 2003
- [2] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, New York, 2002).
- [3] M. P. Allen and J. Tildesley, *Computer Simulation of Liquids* (Oxford University, New York, 1987).
- [4] P. J. Hoogerbrugge, J. M. V. A. Koelman. Simulating Microscopic Hydrodynamic Phenomena with Dissipative Particle Dynamics. Euro phys. Lett, 19 (3), pp. 155-160 (1992).
- [5] Hong Liu, Hu-Jun Qian, Ying Zhao, Zhong-Yuan Lu. Dissipative particle dynamics simulation study on the binary mixture phase separation coupled with polymerization. J Chem Phys. 127, 144903 (2007)
- [6] Peter.V. Coveney. Computer simulations of domain growth and phase separation in two-dimensional binary immiscible fluids using dissipative particle dynamics. Phys. Rev. E 54, 5134–5141 (1996)
- [7] Chongli Zhong, Dahuan Liu. Understanding multicompartement micelles using Dissipative particle dynamics simulation. Macromolecular Theory and simulation. Vol 16.issue 2, pages 141-157.
- [8] Live Rekvig, Marieke Kranenburg, Jocelyne Vreede, Bjorn Hafskjold, Berend Smit. Investigation of surfactant efficiency using Dissipative particle dynamics. Langmuir 2003, 19, 8195-8205.
- [9] Robert D. Groot, Patrick B. Warren, Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation. J. Chem. Phys. 107, 4423 (1997).



- [10] Amitesh Maiti, Simon McGrother. Bead–bead interaction parameters in dissipative particle dynamics: Relation to bead-size, solubility parameter, and surface tension, *J. Chem. Phys.* **120**, 1594 (2004).
- [11] K.P.Travis, Mark Bankhead, Kevin Good, Scott L. Owens. New parametrization method for dissipative particle dynamics. *J. Chem. Phys.* **127**, 014109 (2007).
- [12] G. M. Ataev, Anomalous temperature dependence of interfacial tension in water-hydrocarbon mixtures, *Russian J. Phys. Chem. A* **81**, 2094 (2007)
- [13] A. Rafati, E. Ghasemian, and M. Abdolmaleki, Surface Properties of Binary Mixtures of Ethylene Glycol with a Series of Aliphatic Alcohols *J. Chem. Eng Data* **53**, 1944 (2008).
- [14] G. Vázquez, E. Alavez, and M. Navaza, Structural stability of a colloidal solution of  $\text{Ca}(\text{OH})_2$  nanocrystals exposed to high relative humidity conditions *J. Chem. Eng. Data* **40**, 611 (1995)
- [15] D. Villers and J. K. Platten, Temperature dependence of the interfacial tension between water and long-chain alcohols *J. Phys. Chem.* **92**, 4023 (1988)
- [16] E. Mayoral and A. Gamma Goicochea, Modeling the temperature dependent interfacial tension between organic solvents and water using dissipative particle dynamics *J. Chem. Phys.* **138**, 0947013 (2013).
- [17] Himanshu Goel, Rakesh Chandran P, Kishalay Mitra, Saptarshi Majumdar, Partha Ray. Estimation of interfacial tension for immiscible and partially miscible liquid systems by Dissipative Particle Dynamics. *Chemical Physics Letters* **600** (2014) 62–67
- [18] Alfonso Gautieri&Simone Vesentini&Alberto Redaelli. How to predict diffusion of medium-sized molecules in polymer matrices. From atomistic to coarse grain simulations. *J Mol Model* (2010) **16**:1845–1851
- [19] Xin Liu, Sondre K. Schnell, Jean-Marc Simon, Dick Bedeaux, Signe Kjelstrup, Andre Bardow, and Thijs J. H. Vlugt. Fick Diffusion Coefficients of Liquid Mixtures Directly Obtained From Equilibrium Molecular Dynamics. *J. Phys. Chem. B* **2011**, **115**, 12921–12929

- [20] P.Espanol , P. Warren. Statistical mechanics of dissipative particle dynamics. Europhys. Lett. 30 191 (1995).
- [21] J. H. Hildebrand and R. L. Scott, *Regular Solution* (Prentice-Hall, Englewood Cliffs, New York, 1962).
- [22] C. M. Hansen, *Hansen Solubility Parameters* (CRC Press, Taylor and Francis Group, Boca Raton, 2007)
- [23] H. Inaba and K. Sato, A measurement of interfacial tension between tetradecane and ethylene glycol water solution by means of the pendant drop method Fluid Phase Equilibria **125**, 159 (1996).
- [24] M. Alpbaz , A. Bilgesu, and O.Tutkun, The measurement of interfacial tension by Drop weight Method Commun. Fac.Sci.Univ.Ank.SerieB. **34**, 103 (1988).
- [25] S. Zeppieri, J. Rodríguez, and A. L. López de Ramos, Interfacial Tension of Alkane+Water Systems J. Che. Eng. Data **46**, 1086 (2001)
- [26] Shigetoshi Kobuchi, Kenji Ishige. Correlation of Vapor-Liquid Equilibria Using Wilson Equation with Parameters Estimated from Solubility Parameters and Molar Volumes. Mem Fac Eng Yamaguchi Univ. ol. 62 No.1 (2011)
- [27] DPD is a module in the Materials Studio Modeling software package from Accelrys Inc. See [accelrys.com/products/datasheets/dpd.pdf](http://accelrys.com/products/datasheets/dpd.pdf)
- [28] Forcite is a module in the Materials Studio Modeling software package from Accelrys Inc. See [accelrys.com/products/datasheets/forcite-plus.pdf](http://accelrys.com/products/datasheets/forcite-plus.pdf)
- [29] H. Sun. COMPASS: An ab initio force-field optimized for condensed phase applications-overview with details an alkane and benzene compounds. J. Phys. Chem. B, 1998, 102(38), pp 7338-7364.
- [30] G.D. Moggridge. Prediction of the mutual diffusivity in binary non-ideal liquid mixtures from the tracer diffusion coefficients. . Chemical Engineering Science 71 (2012) 226–238.
- [31] David R. Lide. CRC Handbook of chemistry and physics. CRC press. 81st Edition 2000.
- [32] Y. Marcus,G.T. Hefter. The compressibility of liquids at ambient temperature and pressure. Journal of Molecular Liquids 73,74(1997) 61-74.

- [33] L.J. Root, B.J. Berne. Effect of pressure on hydrogen bonding in glycerol: A molecular dynamics investigation. *J. Chem. Phys.* 107 (11), 1997.
- [34] C.L. Yaws. *Chemical Property Handbook*. McGraw\_Hill 1999.
- [35] Don W. Green, Robert H. Perry. *Perry's Chemical Engineers Handbook*. McGRAW\_HILL. 8 th Edition 2008.
- [36] George S. Kell, Density, thermal expansivity, and compressibility of liquid water from 0.deg. to 150.deg *J. Che. Eng. Data* **20**, 97 (1975)
- [37] E. Alcart, G. Tardajos, and M. Díaz Peña, Isothermal Compressibility and Derived Properties of the Benzene + Toluene System at Various Temperatures *J. Che. Eng. Data* **26**, 283 (1981)
- [38] E. Alcart, G. Tardajos, and M. Díaz Peña, Isothermal Compressibility of Cyclohexane + n-Hexane, Cyclohexane + n-Heptane, Cyclohexane + n-Octane, and Cyclohexane + n-Nonane *J. Che. Eng. Data* **25**, 140 (1980)
- [39] Gennadiy I. Egorov, Dmitriy M. Makarov, and Arkadiy M. Kolker, Densities and Volumetric Properties of Ethylene Glycol+Dimethylsulfoxide Mixtures at Temperatures of (278.15 to 323.15) K and Pressures of (0.1 to 100)MPa *J. Che. Eng. Data* **55**, 3481 (2010)
- [40] E. Alcart, G. Tardajos, and M. Díaz Peña, Isothermal Compressibility of Cyclohexane-n-Decane, Cyclohexane-n-Dodecane, and Cyclohexane-n-Tetradecane *J. Che. Eng. Data* **26**, 22 (1981)